

## ATTACHMENT 3

Rio Grande Silver Bulldog Mine Treatment Summary

Water Quality Analytical Results of Final Effluent

Site Specific Tiered Standards Segments 4a and 7 from CCR 1002-36

Site Specific Standards are in place for Windy Gulch, Willow Creek and Rio Grande 4a.

A 5-year extension on the effective dates for Tier 1 and Tier 2 Standards is in process and are expected to be approved by the WQCC in October 2023.

# **Rio Grande Silver Bulldog Mine Treatment Summary**

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**May 5, 2023**

CONFIDENTIAL

## Introduction

WaterTectonics conducted a mine water treatability study for the Hecla Bulldog Mine facility near Creede, Colorado. This treatability study tested the efficacy of the treatability process proposed by WaterTectonics in a February 6, 2023, proposal (Figure 1). This process included oxidation, filtration, pH adjustment, greensand filtration, and polishing filtration for metals. The goals of this treatability study were to meet the worst-case effluent discharge limits provided in Table 1. The results of the WET testing report from April 6, 2023 indicated zero survival in the final effluent because of residual chlorine from the oxidation step in the process. The full process was retested optimizing the initial dose of sodium hypochlorite and adding granular activated carbon (GAC) after the greensand filter to remove residual chlorine.

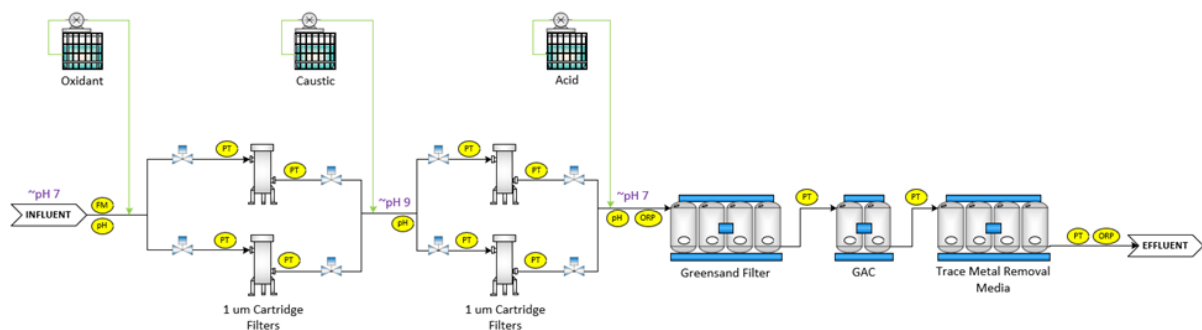


Figure 1 Proposed process flow diagram.

Table 1. Worst case influent concentrations, probable average influent concentrations, worst case effluent discharge limits

Parameters	Units	Worst Case Influent	Probable Average Influent (50/50)	Worst Case Effluent Discharge Limit
pH	s.u.	6.59	7.04	6.5-9
Sulfate	mg/L	146	77	NA
Nitrate	mg/L	?	0.17	100
Hardness	mg/L	30 to 126	77	
Fluoride	mg/L	0.46	0.27	2
Alkalinity	mg/L	?	78	
Aluminum, Total Recoverable	mg/L	0.65	0.316	0.36
Arsenic, Total Recoverable	mg/L	0.035	0.029	0.0016
Cadmium, Dissolved	mg/L	0.0076	0.0028	0.0059
Copper, Dissolved	mg/L	0.0047	0.0013	0.006

Parameters	Units	Worst Case Influent	Probable Average Influent (50/50)	Worst Case Effluent Discharge Limit
Iron, Dissolved	mg/L	1.3	0.54	NA
Iron, Total Recoverable	mg/L	7.1	3.65	1.0
Lead, Dissolved	mg/L	0.0036	0.00140	0.00168
Manganese, Dissolved	mg/L	3	1.49	1.39
Mercury, Total	ng/L	29	12.2	10
Zinc, Dissolved	mg/L	1.1	0.55	1.56
Selenium	mg/L	0.0077	0.0035	0.0046

Highlighted values in red above worst case effluent discharge limits.

## Method

Twelve, five-gallon containers of mine water were received by WaterTectonics on March 6, 2023. The samples were immediately refrigerated. pH, ORP, DO conductivity, and turbidity were measured in all 12 containers. The same parameters were measured for all process steps.

### Oxidation, filtration and pH adjustment

Oxidation, filtration, and pH adjustment were initially tested at bench scale using small volume samples collected from 1 of the 12 containers. 7.85% sodium hypochlorite was used for oxidation testing. Filtration was tested using 1.5 µm Whatman Grade 934-AH Glass Microfiber Filters with vacuum filtration apparatus before pH adjustment. pH was raised with sodium hydroxide. A pH range between 8.8 - 9.4 was tested to determine optimal pH to remove iron and zinc after a second 1.5 µm filtration step.

10 liters from each container was composited in a 55-gallon barrel prior to the larger scale lab testing required for the column tests.

### Greensand

pH was lowered to 6.8 with sulfuric acid prior to greensand filtration. Greensand was tested at 5 gpm/ft<sup>2</sup> in a 2" column with a 30" bed depth. The greensand was preconditioned by soaking overnight with sodium hypochlorite and backflushed to remove fines and residual chlorine. The column was forward flushed with tap water and drained to just above the greensand before testing the mine water. 20 liters of pretreated mine water was filtered through the column before collecting an additional 20 liters for analytical testing and additional media filtration targeting metals removal.

### Granular Activated Carbon (GAC)

Acid washed virgin coconut shell GAC was added to a column, soaked overnight, and backwashed with tap water until clear. Following filtration, the water was treated with a 30" bed depth of GAC in a 2" diameter column at 5 gpm/ft<sup>2</sup>.

## Metsorb

Greensand effluent was treated with MetSorb™ HMRG at 8 gpm/ft<sup>2</sup> in a 2" column with a 30" bed depth. The column was backflushed to remove fines prior to processing the sample. 15 liters of greensand effluent was treated through the Metsorb prior to sampling for analytical testing.

Samples were tested for the parameters listed in Appendix A.

## Results

### Influent Characterization

pH, ORP, DO, conductivity and turbidity were consistent across all 12 containers (Table 2). ORP was slow to stabilize and drifted down over the course of measuring the 12 containers.

**Table 2. In-house influent container characterization**

Container	pH	ORP (mV)	Dissolved Oxygen (mg/L)	Conductivity (µS/cm)	Turbidity (NTU)
1	6.64	337.6	6.3	367	44.9
2	6.8	334	7.44	364	42.5
3	6.75	327	6.66	350	41.5
4	6.69	319.4	6.57	367	46.1
5	6.71	318.5	6.43	351	37.8
6	6.74	317.3	7.38	358	39.2
7	6.73	311.8	7.56	356	41.4
8	6.73	309.1	7.62	366	36.7
9	6.76	305.9	7.74	349	36.6
10	6.74	303.5	7.25	378	46.5
11	6.75	301.8	6.85	372	46.6
12	6.73	299.6	6.72	372	48.2

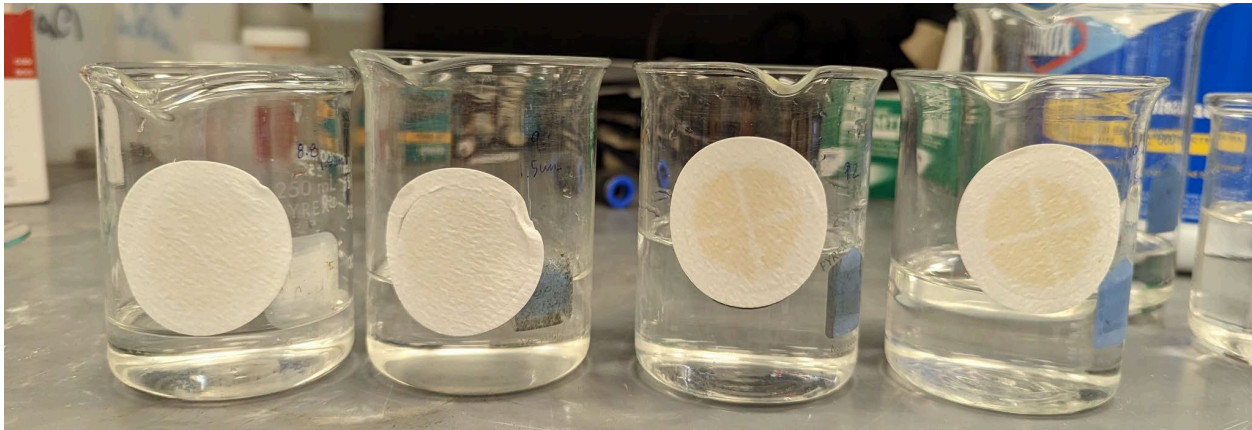
### pH Optimization Testing

The initial sodium hypochlorite dosing was estimated based on the expected chlorine demand for greensand treatment using catalytic oxidation and the probable average influent iron and manganese concentrations. 16 mg/L sodium hypochlorite was dosed with a minimal reaction time prior to 1.5 µm filtration. The oxidized sample filtered easily leaving a dark iron color on the filters (Figure 2). Iron concentrations were reduced from 7.5 mg/L to 0.1 mg/L after oxidation and 1.5 µm filtration, measured using a Hach colorimetric method (Table 3). The filters after pH adjustment showed an increasing concentration of solids were collected as the pH was raised from 8.8 to 9.4 (Figure 3). The sample with pH adjusted to 9.2 had the lowest turbidity after 1.5 µm filtration. Iron and zinc were also non-detect in the

pH 9.2 treatment after 1.5  $\mu$ m filtration. pH 9.2 was selected as the best pH to remove iron, zinc, and other metals.



**Figure 2.** 1.5  $\mu$ m filter after oxidation



**Figure 3.** 1.5  $\mu$ m filters after pH adjustment from left to right: pH 8.8, pH 9.0, pH 9.2, pH 9.4

**Table 3.** pH adjustment treatment optimization testing

Bull Dog Sample Jug 1	Units	16 mg/L bleach > 1.5 $\mu$ m filter	pH 8.8 > 1.5 $\mu$ m filter	pH 9.0 > 1.5 $\mu$ m filter	pH 9.2 > 1.5 $\mu$ m filter	pH 9.4 > 1.5 $\mu$ m filter
pH	s.u.	6.85	8.63	8.84	9.19	9.31
Conductivity	$\mu$ S/cm	401	490	503	514	528
Turbidity	NTU	0.53	0.41	0.53	0.3	0.58
DO	mg/L	7.87	8.7	8.35	8.49	8.42
ORP	mV	668.1	424.6	378.2	316.8	339.1
Iron	mg/L	0.11	0.02	0.03	ND < 0.02	0.02
Zinc	mg/L	0.61	0.03	0.07	ND < 0.01	ND < 0.01

## Full Process Testing

10 liters of sample was collected from each container to make a 120L sample. 0.2 mL/L 7.85% sodium hypochlorite was dosed raising the ORP from 418 to 614 mV (Table 4). The sample was mixed 5-10 minutes by recirculating with a pump prior to analytical sample collection and filtering through a 1  $\mu$ m melt blown



polypropylene filter to a second clean barrel. The pH was adjusted to 9.2 with 0.063 mL 50% NaOH per liter. The sample was mixed briefly by recirculating with a pump prior to analytical sample collection and filtering through another 1  $\mu$ m melt blown polypropylene filter to a third clean barrel. Analytical samples were collected after the pH 9.2 > 1  $\mu$ m filtration step. All parameters aside from pH were below the worst case effluent discharge limits after the pH 9.2 > 1.0  $\mu$ m filtration step (Table 5). The pH was adjusted from 9.2 to 6.8 with 0.03 mL 96% sulfuric acid per liter before greensand filtration. The inlet pressure of the greensand column increased from 5 PSI after 5 gallons treated to 10 PSI after 10 gallons treated indicating that the filter was capturing solids. All metals with effluent discharge limits except for mercury were non-detect after greensand filtration. All metals were non-detect after the Metsorb filtration.

Iron slowly oxidized passing through the 1  $\mu$ m filtration step before raising the pH to 9.2. Figure 4 and Figure 5 photos were taken 6 hours apart. Iron was observed oxidizing in the samples with an extended reaction time. The settled solids in samples collected after the pH was raised to 9.2 before and after 1.5  $\mu$ m filtration indicated that some iron and manganese continued to oxidize after filtration (Figure 6). The first filter after oxidation had an orange color and the second filter after pH was raised to 9.2 had a darker brown color (Figure 7).



**Figure 4.** Bulldog mine treated samples at initial sample collection from left to right: influent, oxidant > 1  $\mu$ m, pH 9.2, pH 9.2 > 1  $\mu$ m



**Figure 5.** Bulldog mine treated samples 6 hours after initial testing from left to right: influent, oxidant > 1  $\mu$ m, pH 9.2, pH 9.2 > 1  $\mu$ m, pH 6.8

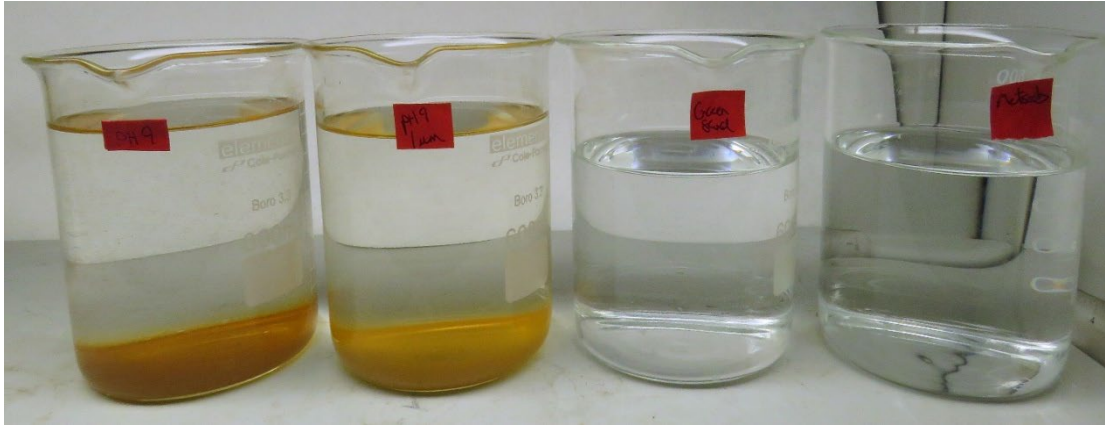


Figure 6. Samples from left to right: pH 9.2, pH 9.2 > 1.5  $\mu$ m filtration, greensand effluent, Metsorb effluent



Figure 7. Filters after testing, Oxidant > 1  $\mu$ m (left), pH 9.2 > 1  $\mu$ m (right)

Aluminum was non-detect in the influent and below the probable average influent concentration. The treatment system as proposed is expected to remove particulate aluminum in the first 1  $\mu$ m filtration



step at the expected neutral pH of the influent mine water. Aluminum that isn't removed in the first filtration step is expected to be removed by the Metsorb metal polishing media.

Arsenic was below the probable average influent concentration in the influent but above the expected discharge limit. Arsenic concentrations were reduced slightly after oxidation and 1  $\mu\text{m}$  filtration and below the expected discharge limit after adjusting the pH to 9.2 and 1  $\mu\text{m}$  filtration. The treatment system as proposed is expected to remove arsenic concentrations as high as the expected worst case influent.

Dissolved cadmium was at the worst-case concentration in the influent. Overall total cadmium decreased but the dissolved cadmium concentration increased slightly after oxidation and 1  $\mu\text{m}$  filtration. Dissolved cadmium was below the discharge limit in the pH 9.2 sample after 1  $\mu\text{m}$  filtration. Total and dissolved cadmium were non-detect in the greensand effluent and Metsorb effluent samples.

Copper was non-detect in all samples and was not expected to be above the discharge limit in the influent. Copper up to the worst-case influent concentration isn't expected to exceed the worst case effluent discharge limit or affect removal of other parameters.

Total iron in the influent was higher than the worst-case concentration. The total iron concentration was reduced following oxidation and 1  $\mu\text{m}$  filtration but still above the discharge limit. Total iron was below the discharge limit in the pH 9.2 sample with 1  $\mu\text{m}$  filtration. Total and dissolved iron were non-detect in the greensand and Metsorb effluent samples.

Dissolved lead was non-detect and below the effluent discharge limit in all samples. Total lead was detected in the influent and non-detect in all other samples. The treatment system as proposed is expected to remove lead concentrations as high as the worst-case influent concentration.

The influent dissolved manganese concentration was between the probable average and worst-case concentrations. Overall manganese was removed as expected through the process. Total and dissolved manganese were both non-detect in the Greensand and Metsorb effluent samples.

Total and dissolved mercury were non-detect ( $< 0.5 \text{ ng/L}$ ) in the influent sample. Mercury was detected in the oxidant  $> 1 \text{ }\mu\text{m}$ , pH 9.2  $> 1 \text{ }\mu\text{m}$  and greensand effluent samples well below the 10 ng/L worst case effluent discharge limit. 3.22 ng/L total mercury in the greensand effluent was reduced to non-detect concentrations in the Metsorb effluent.

The influent dissolved zinc concentration was between the probable average and worst case concentrations. Dissolved zinc was non-detect in the pH 9.2 sample with 1  $\mu\text{m}$  filtration but some total zinc remained. Total and dissolved zinc were both non-detect in the greensand and Metsorb effluent samples.

Selenium was below the discharge effluent limit and non-detect in all samples. Selenium reduction is not expected in this treatment process. Although water at the worst-case influent concentration may exceed potential discharge limits, the low concentration results of the March and April 2023 influent samples indicate that the expected influent concentrations will be below discharge limits and not require treatment.

TSS increased after oxidation which was expected as ferrous iron was converted to insoluble ferric iron. 1  $\mu\text{m}$  filtration after oxidation removed 55% of the TSS in the oxidation sample. Both TSS and turbidity decreased after the oxidation > 1  $\mu\text{m}$  and pH 9.2 > 1  $\mu\text{m}$  process steps. TSS was non-detect in the Metsorb effluent.

Nitrate was barely above detection in both samples tested and well below the worst-case effluent discharge limit.



Table 4. Bulldog Mine treatability in-house analytical testing

Parameter	Units	Influent 03/2023	Oxidant Effluent	Oxidant > 1 µm	pH 9.2	pH 9.2 > 1 µm	Greensand Effluent	Metsorb Effluent	Worst Case Effluent Discharge Limit
pH	s.u.	6.29	6.64	6.84	9.21	9.2	6.82	7.03	6.5-9
Conductivity	µS/cm	361	407	409	466	466	513	1070	-
Turbidity	NTU	63.3	39.9	17.7	4.94	0.81	0.21	0.19	-
Dissolved Oxygen	mg/L	10.28	10.33	10.92	9.62	9.59	9.44	9.46	-
ORP	mV	417.5	614	598.6	155.5	176.9	> 500	424	-

Table 5. Bulldog mine treatability third party analytical testing

Parameter	Units	Influent 03/2023	Oxidant Effluent	Oxidant > 1 µm	pH 9.2	pH 9.2 > 1 µm	Greensand Effluent	Metsorb Effluent	Worst Case Effluent Discharge Limit
TSS	mg/L	16	27	12	8.0	5.0	ND < 4.0	ND < 4.0	-
Sulfate	mg/L	62	-	-	-	-	-	26	NA
Nitrate	mg/L	0.053	-	-	-	-	-	0.053	100
Hardness	mg CaCO <sub>3</sub> /L	156	-	-	-	-	-	457	-
Fluoride	mg/L	0.38	-	-	-	-	-	0.13	2
Alkalinity, Total	mg CaCO <sub>3</sub> /L	120	-	-	-	-	-	14	-
Alkalinity, bicarbonate	mg CaCO <sub>3</sub> /L	120	-	-	-	-	-	14	-
Alkalinity, carbonate	mg CaCO <sub>3</sub> /L	ND < 2.0	-	-	-	-	-	ND < 2.0	-
Alkalinity, Hydroxide	mg CaCO <sub>3</sub> /L	ND < 2.0	-	-	-	-	-	ND < 2.0	-
Aluminum, Total	mg/L	ND < 0.100	-	ND < 0.100	-	ND < 0.100	ND < 0.100	ND < 0.100	0.36
Aluminum, Dissolved	mg/L	ND < 0.110	-	ND < 0.110	-	ND < 0.110	ND < 0.110	ND < 0.110	-
Arsenic, Total	mg/L	0.013	-	0.0025	-	0.0012	ND < 0.0011	ND < 0.0011	0.0016
Arsenic, Dissolved	mg/L	0.0013	-	ND < 0.001	-	ND < 0.001	ND < 0.001	ND < 0.001	-
Cadmium, Total	mg/L	0.0210	-	0.019	-	0.0091	ND < 0.0044	ND < 0.0044	-

Parameter	Units	Influent 03/2023	Oxidant Effluent	Oxidant > 1 µm	pH 9.2	pH 9.2 > 1 µm	Greensand Effluent	Metsorb Effluent	Worst Case Effluent Discharge Limit
Cadmium, Dissolved	mg/L	0.0076	-	0.017	-	ND < 0.004	ND < 0.004	ND < 0.004	0.0059
Calcium, Total	mg/L	58	-	52	-	52	49	180	-
Calcium, Dissolved	mg/L	52	-	52	-	51	51	210	-
Copper, Total	mg/L	ND < 0.0044	-	ND < 0.0044	-	ND < 0.0044	ND < 0.0044	ND < 0.0044	-
Copper, Dissolved	mg/L	ND < 0.004	-	ND < 0.004	-	ND < 0.004	ND < 0.004	ND < 0.004	0.006
Iron, Total	mg/L	9.10	-	1.40	-	0.67	ND < 0.050	ND < 0.050	1.0
Iron, Dissolved	mg/L	0.78	-	0.10	-	ND < 0.056	ND < 0.056	ND < 0.056	NA
Lead, Total	mg/L	0.0089	-	ND < 0.0011	-	ND < 0.0011	ND < 0.0011	ND < 0.0011	-
Lead, Dissolved	mg/L	ND < 0.001	-	ND < 0.001	-	ND < 0.001	ND < 0.001	ND < 0.001	0.00168
Magnesium, Total	mg/L	2.6	-	2.4	-	2.3	2.2	1.6	-
Manganese, Total	mg/L	2.7	-	2.5	-	1.8	ND < 0.010	ND < 0.010	-
Manganese, Dissolved	mg/L	2.4	-	2.2	-	0.95	ND < 0.011	ND < 0.011	1.39
Mercury, Total	ng/L	ND < 0.5	-	1.73	-	1.06	3.22	ND < 0.5	10
Mercury, Dissolved	ng/L	ND < 0.5	-	0.639	-	0.72	3.31	ND < 0.5	-
Zinc, Total	mg/L	1.1	-	0.98	-	0.32	ND < 0.050	ND < 0.050	-
Zinc, Dissolved	mg/L	0.8	-	0.99	-	ND < 0.056	ND < 0.056	ND < 0.056	1.56
Selenium, Total	mg/L	ND < 0.0044	-	ND < 0.0044	-	ND < 0.0044	ND < 0.0044	ND < 0.0044	0.0046

ND = The parameter was analyzed for, but was not detected above the reported sample quantitation limit



## Particle Size Distribution

The number weighted mean particle size was 0.78  $\mu\text{m}$  in the influent (Table 6). The volume weighted mean in the influent was 27.15  $\mu\text{m}$  (Table 7). Mean particle size was greater than 1  $\mu\text{m}$  in the 1  $\mu\text{m}$  filtered samples which indicates particles formed as iron and manganese oxidized after filtration.

**Table 6. Cumulative number % less than size ( $\mu\text{m}$ )**

Sample	10th Percentile	50th Percentile	90th Percentile	Number Weighted Mean
Influent	0.53	0.62	0.89	0.78
Oxidant Effluent	0.54	0.76	2.46	1.35
Oxidant > 1 $\mu\text{m}$	0.64	2.73	12.92	5.05
pH 9 Effluent	0.62	1.45	5.7	2.69
pH 9 > 1 $\mu\text{m}$	0.56	1.03	5.21	2.18

**Table 7. Cumulative volume % less than size ( $\mu\text{m}$ )**

Sample	10th Percentile	50th Percentile	90th Percentile	Volume Weighted Mean
Influent	8.67	21.24	56.48	27.15
Oxidant Effluent	5.32	12.65	24.7	15.32
Oxidant > 1 $\mu\text{m}$	10.19	18.99	32.04	21.62
pH 9 Effluent	9.98	25.18	62.84	33.56
pH 9 > 1 $\mu\text{m}$	6.26	13.88	26.9	15.57

## Process Retest with Granular Activated Carbon

GAC was added to the process after the effluent test submitted to SeaCrest Group did not pass WET testing because of residual chlorine. The full process was retested with GAC added between the greensand and Metsorb steps. The new sample had similar pH and turbidity compared to the previous sample (Table 8). Mercury concentrations were higher than the previous sample but still lower than the historical average concentration (Table 9). Chlorine demand using the greensand catalytic oxidation process was estimated to be 17.05 mg/L  $\text{Cl}_2$  based in in-house iron and manganese measurements. The sodium hypochlorite was dosed in a barrel and mixed for 5 minutes before 1  $\mu\text{m}$  filtration. Free chlorine was 10.3 mg/L after the 1  $\mu\text{m}$  filtration step. Residual chlorine was non-detect (< 0.02 mg/L) after the GAC filtration step. All metals were non-detect in the Metsorb effluent.



**Table 8. Bulldog mine treatability retest in-house analytical testing**

Parameter	Units	Influent 03/2023	Influent 04/2023	Metsorb Effluent	Worst Case Effluent Discharge Limit
pH	s.u.	6.29	6.92	6.8	6.5-9
Conductivity	uS/cm	361	318	370	
Turbidity	NTU	63.3	60.8	.29	
Dissolved Oxygen	mg/L	10.28	11.22	11.49	
ORP	mV	417.5	420	468	

**Table 9. Bulldog mine treatability retest third party analytical testing**

Parameter	Units	Influent 03/2023	Influent 04/2023	Metsorb Effluent	Worst Case Effluent Discharge Limit
TSS	mg/L	16	21	ND < 4	
Sulfate	mg/L	62	59	110	NA
Nitrate as N	mg/L		0.087	ND < 0.050	100
Hardness	mg CaCO <sub>3</sub> /L	156	124	95	
Fluoride	mg/L	0.38	0.36	0.26	2
Alkalinity, Total	mg CaCO <sub>3</sub> /L	120	110	20	
Alkalinity, bicarbonate	mg CaCO <sub>3</sub> /L	120	110	20	
Alkalinity, carbonate	mg CaCO <sub>3</sub> /L	ND < 2.0	ND < 2.0	ND < 2.0	
Alkalinity, Hydroxide	mg CaCO <sub>3</sub> /L	ND < 2.0	ND < 2.0	ND < 2.0	
Aluminum, Total	mg/L	ND < 0.100	ND < 0.100	ND < 0.100	0.36
Aluminum, Dissolved	mg/L	ND < 0.110	ND < 0.100	ND < 0.110	
Arsenic, Total	mg/L	0.013	0.017	ND < 0.0016	0.0016
Arsenic, Dissolved	mg/L	0.0013	ND < 0.0016	ND < 0.0016	
Cadmium, Total	mg/L	0.0210	0.020	ND < 0.0044	
Cadmium, Dissolved	mg/L	0.0076	0.006	ND < 0.004	0.0059
Calcium, Total	mg/L	58	46	38	
Calcium, Dissolved	mg/L	52	46	39	
Copper, Total	mg/L	ND < 0.0044	0.0064	ND < 0.006	
Copper, Dissolved	mg/L	ND < 0.004	ND < 0.006	ND < 0.006	0.006
Iron, Total	mg/L	9.10	9.6	ND < 0.050	1.0
Iron, Dissolved	mg/L	0.78	0.11	ND < 0.056	NA
Lead, Total	mg/L	0.0089	0.011	ND < 0.0011	
Lead, Dissolved	mg/L	ND < 0.001	ND < 0.001	ND < 0.001	0.00168
Magnesium, Total	mg/L	2.6	2.2	ND < 1	

Magnesium, Dissolved	mg/L	2.4	2.3	ND < 1.1	
Manganese, Total	mg/L	2.7	2.3	ND < 0.010	
Manganese, Dissolved	mg/L	2.4	2.2	ND < 0.011	1.39
Mercury, Total	ng/L	ND < 0.5	3.12	ND < 0.5	10
Mercury, Dissolved	mg/L	ND < 0.5	0.511	ND < 0.5	
Zinc, Total	mg/L	1.1	0.86	ND < 0.050	
Zinc, Dissolved	mg/L	0.8	0.54	ND < 0.056	1.56
Selenium, Total	mg/L	ND < 0.0044	ND < 0.0046	ND < 0.0046	0.0046
Selenium, Dissolved	mg/L	ND < 0.004	ND < 0.0046	ND < 0.0046	

## Conclusions

The proposed process effectively met all worst-case discharge requirements in the sample as tested. The treatment system as proposed is expected to meet all worst-case effluent discharge limits with influent concentrations as high as the worst-case influent concentrations included in the RFP. The original sample did not pass the WET test. Granular activated carbon was added to remove residual chlorine after greensand. A new sample was treated and delivered to Seacrest for WET testing. The new sample passed the WET test.

## Appendix A – Analytical Test Methods and Detection Limits

**Table A. Water Tectonics analytical test methods and detection limits**

Parameter	Unit	Method	Detection Limit
pH	standard units	Hach HQ40d meter	N/A
ORP	mV	Hach HQ40d meter	N/A
Conductivity	µS/cm	Hach HQ40d meter	N/A
Turbidity	NTU	Hach 2100P meter	0.01
Dissolved Oxygen	mg/L	Hach HQ40d meter	0.1

**Table B Third party laboratory test methods and detection limits.**

Parameter	Units	Method	Detection Limit
TSS	mg/L	SM 2540D	4
Sulfate	mg/L	ASTM D516-11	10 - 20
Nitrate	mg/L	EPA 353.2	Pending
Hardness	mg/L	SM 2340B	20
Fluoride	mg CaCO <sub>3</sub> /L	SM 4500-F C	0.02
Alkalinity, Total	mg CaCO <sub>3</sub> /L	SM 2320B	2.0
Alkalinity, bicarbonate	mg CaCO <sub>3</sub> /L	SM 2320B	2.0
Alkalinity, carbonate	mg CaCO <sub>3</sub> /L	SM 2320B	2.0
Alkalinity, Hydroxide	mg CaCO <sub>3</sub> /L	SM 2320B	2.0
Aluminum, Total	mg/L	EPA 6010D	0.100
Aluminum, Dissolved	mg/L	EPA 6010D	0.110
Arsenic, Total	mg/L	EPA 200.8	0.0011
Arsenic, Dissolved	mg/L	EPA 200.8	0.001
Cadmium, Total	mg/L	EPA 200.8	0.0044
Cadmium, Dissolved	mg/L	EPA 200.8	0.004
Calcium, Total	mg/L	EPA 6010D	5
Calcium, Dissolved	mg/L	EPA 6010D	1.1
Copper, Total	mg/L	EPA 200.8	0.0044
Copper, Dissolved	mg/L	EPA 200.8	0.004
Iron, Total	mg/L	EPA 6010D	0.250
Iron, Dissolved	mg/L	EPA 6010D	0.056
Lead, Total	mg/L	EPA 200.8	0.0011
Lead, Dissolved	mg/L	EPA 200.8	0.001
Magnesium, Total	mg/L	EPA 6010D	1
Manganese, Total	mg/L	EPA 6010D	0.01
Manganese, Dissolved	mg/L	EPA 6010D	0.011
Mercury, Total	ng/L	EPA 1631	Pending
Mercury, Dissolved	ng/L	EPA 1631	Pending

Parameter	Units	Method	Detection Limit
Zinc, Total	mg/L	EPA 6010D	0.32
Zinc, Dissolved	mg/L	EPA 6010D	0.056
Selenium, Total	mg/L	EPA 200.8	0.0044

May 22, 2023

Report to:

Randy McClure  
Rio Grande Silver, Inc.  
112 E. 12th St.  
Creede, CO 81130

Bill to:

Randy McClure  
Rio Grande Silver, Inc.  
P.O. Box 610  
Creede, CO 81130

Project ID:

ACZ Project ID: L80005

Randy McClure:

Enclosed are the analytical results for sample(s) submitted to ACZ Laboratories, Inc. (ACZ) on April 21, 2023. This project has been assigned to ACZ's project number, L80005. Please reference this number in all future inquiries.

All analyses were performed according to ACZ's Quality Assurance Plan. The enclosed results relate only to the samples received under L80005. Each section of this report has been reviewed and approved by the appropriate Laboratory Supervisor, or a qualified substitute.

Except as noted, the test results for the methods and parameters listed on ACZ's current NELAC certificate letter (#ACZ) meet all requirements of NELAC.

This report shall be used or copied only in its entirety. ACZ is not responsible for the consequences arising from the use of a partial report.

All samples and sub-samples associated with this project will be disposed of after June 21, 2023. If the samples are determined to be hazardous, additional charges apply for disposal (typically \$11/sample). If you would like the samples to be held longer than ACZ's stated policy or to be returned, please contact your Project Manager or Customer Service Representative for further details and associated costs. ACZ retains analytical raw data reports for ten years.

If you have any questions or other needs, please contact your Project Manager.



Sue Webber has reviewed and  
approved this report.





**Rio Grande Silver, Inc.**

Project ID:

Sample ID: EFFLUENT

ACZ Sample ID: **L80005-01**

Date Sampled: 04/20/23 12:00

Date Received: 04/21/23

Sample Matrix: Waste Water

## Inorganic Prep

Parameter	EPA Method	Dilution	Result	Qual	XQ	Units	MDL	PQL	Date	Analyst
Lab Filtration (0.45um) & Acidification	M200.7/200.8/3005A								04/26/23 15:00	mlh
Total Recoverable Digestion	M200.2 ICP-MS								05/01/23 18:00	scp

## Metals Analysis

Parameter	EPA Method	Dilution	Result	Qual	XQ	Units	MDL	PQL	Date	Analyst
Aluminum, total recoverable	M200.8 ICP-MS	1	<0.005	U		mg/L	0.005	0.015	05/02/23 18:34	scp
Arsenic, total recoverable	M200.8 ICP-MS	1	<0.0002	U		mg/L	0.0002	0.001	05/02/23 18:34	scp
Cadmium, dissolved	M200.8 ICP-MS	1	<0.00005	U		mg/L	0.00005	0.00025	05/11/23 16:21	gjl/scp
Calcium, dissolved	M200.7 ICP	1	43.0			mg/L	0.1	0.5	05/02/23 18:37	wtc
Copper, dissolved	M200.8 ICP-MS	1	0.00119	B		mg/L	0.0008	0.002	05/11/23 16:21	gjl/scp
Iron, dissolved	M200.8 ICP-MS	1	0.0085	B	*	mg/L	0.007	0.02	05/18/23 16:58	kja
Iron, total recoverable	M200.8 ICP-MS	1	<0.007	U	*	mg/L	0.007	0.02	05/02/23 18:34	scp
Lead, dissolved	M200.8 ICP-MS	1	<0.0001	U		mg/L	0.0001	0.0005	05/11/23 16:21	gjl/scp
Magnesium, dissolved	M200.7 ICP	1	0.45	B		mg/L	0.2	1	05/02/23 18:37	wtc
Manganese, dissolved	M200.8 ICP-MS	1	0.00101	B		mg/L	0.0004	0.002	05/11/23 16:21	gjl/scp
Mercury, total	M1631E, Atomic Fluorescence	1	<0.3	U		ng/L	0.3	1	04/25/23 11:31	mlh
Selenium, total recoverable	M200.8 ICP-MS	1	0.00239			mg/L	0.0001	0.00025	05/02/23 18:34	scp
Zinc, dissolved	M200.8 ICP-MS	1	<0.006	U		mg/L	0.006	0.015	05/11/23 16:21	gjl/scp

## Wet Chemistry

Parameter	EPA Method	Dilution	Result	Qual	XQ	Units	MDL	PQL	Date	Analyst
Alkalinity as CaCO3	SM2320B - Titration									
Bicarbonate as CaCO3		1	22.6			mg/L	2	20	05/03/23 0:00	jck
Carbonate as CaCO3		1	<2	U		mg/L	2	20	05/03/23 0:00	jck
Hydroxide as CaCO3		1	<2	U		mg/L	2	20	05/03/23 0:00	jck
Total Alkalinity		1	22.6			mg/L	2	20	05/03/23 0:00	jck
Fluoride	SM4500F-C	1	0.22	B		mg/L	0.15	0.35	05/15/23 13:27	jck
Hardness as CaCO3 (dissolved)	SM2340B - Calculation		109			mg/L	0.2	5	05/22/23 0:00	calc
Lab Filtration (0.45um filter)	SOPWC050	1							04/27/23 8:10	mlh
Nitrate as N	Calculation: NO3NO2 minus NO2		<0.02	UH		mg/L	0.02	0.1	05/22/23 0:00	calc
Nitrate/Nitrite as N	M353.2 - Automated Cadmium Reduction	1	<0.02	UH	*	mg/L	0.02	0.1	04/25/23 23:43	pjb
Nitrite as N	M353.2 - Automated Cadmium Reduction	1	<0.01	UH	*	mg/L	0.01	0.05	04/25/23 23:43	pjb
pH (lab)	SM4500H+ B									
pH		1	7.7	H		units	0.1	0.1	05/03/23 0:00	jck
pH measured at		1	24.6			C	0.1	0.1	05/03/23 0:00	jck
Sulfate	D516-02/-07/-11 - TURBIDIMETRIC	5	152		*	mg/L	5	25	05/10/23 11:06	gkk

**Rio Grande Silver, Inc.**

Project ID:

Sample ID: TRIP BLANK

ACZ Sample ID: **L80005-02**

Date Sampled: 04/20/23 00:00

Date Received: 04/21/23

Sample Matrix: Waste Water

Metals Analysis

Parameter	EPA Method	Dilution	Result	Qual	XQ	Units	MDL	PQL	Date	Analyst
Mercury, total	M1631E, Atomic Fluorescence	1	<0.3	U		ng/L	0.3	1	04/25/23 11:35	mlh



## Report Header Explanations

<i>Batch</i>	A distinct set of samples analyzed at a specific time
<i>Found</i>	Value of the QC Type of interest
<i>Limit</i>	Upper limit for RPD, in %.
<i>Lower</i>	Lower Recovery Limit, in % (except for LCSS, mg/Kg)
<i>MDL</i>	Method Detection Limit. Same as Minimum Reporting Limit unless omitted or equal to the PQL (see comment #5). Allows for instrument and annual fluctuations.
<i>PCN/SCN</i>	A number assigned to reagents/standards to trace to the manufacturer's certificate of analysis
<i>PQL</i>	Practical Quantitation Limit. Synonymous with the EPA term "minimum level".
<i>QC</i>	True Value of the Control Sample or the amount added to the Spike
<i>Rec</i>	Recovered amount of the true value or spike added, in % (except for LCSS, mg/Kg)
<i>RPD</i>	Relative Percent Difference, calculation used for Duplicate QC Types
<i>Upper</i>	Upper Recovery Limit, in % (except for LCSS, mg/Kg)
<i>Sample</i>	Value of the Sample of interest

## QC Sample Types

<i>AS</i>	Analytical Spike (Post Digestion)	<i>LCSWD</i>	Laboratory Control Sample - Water Duplicate
<i>ASD</i>	Analytical Spike (Post Digestion) Duplicate	<i>LFB</i>	Laboratory Fortified Blank
<i>CCB</i>	Continuing Calibration Blank	<i>LFM</i>	Laboratory Fortified Matrix
<i>CCV</i>	Continuing Calibration Verification standard	<i>LFMD</i>	Laboratory Fortified Matrix Duplicate
<i>DUP</i>	Sample Duplicate	<i>LRB</i>	Laboratory Reagent Blank
<i>ICB</i>	Initial Calibration Blank	<i>MS</i>	Matrix Spike
<i>ICV</i>	Initial Calibration Verification standard	<i>MSD</i>	Matrix Spike Duplicate
<i>ICSAB</i>	Inter-element Correction Standard - A plus B solutions	<i>PBS</i>	Prep Blank - Soil
<i>LCSS</i>	Laboratory Control Sample - Soil	<i>PBW</i>	Prep Blank - Water
<i>LCSSD</i>	Laboratory Control Sample - Soil Duplicate	<i>PQV</i>	Practical Quantitation Verification standard
<i>LCSW</i>	Laboratory Control Sample - Water	<i>SDL</i>	Serial Dilution

## QC Sample Type Explanations

Blanks	Verifies that there is no or minimal contamination in the prep method or calibration procedure.
Control Samples	Verifies the accuracy of the method, including the prep procedure.
Duplicates	Verifies the precision of the instrument and/or method.
Spikes/Fortified Matrix	Determines sample matrix interferences, if any.
Standard	Verifies the validity of the calibration.

## ACZ Qualifiers (Qual)

B	Analyte concentration detected at a value between MDL and PQL. The associated value is an estimated quantity.
H	Analysis exceeded method hold time. pH is a field test with an immediate hold time.
L	Target analyte response was below the laboratory defined negative threshold.
U	The material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantitation limit or the sample detection limit.

## Method References

(1)	EPA 600/4-83-020. Methods for Chemical Analysis of Water and Wastes, March 1983.
(2)	EPA 600/R-93-100. Methods for the Determination of Inorganic Substances in Environmental Samples, August 1993.
(3)	EPA 600/R-94-111. Methods for the Determination of Metals in Environmental Samples - Supplement I, May 1994.
(4)	EPA SW-846. Test Methods for Evaluating Solid Waste.
(5)	Standard Methods for the Examination of Water and Wastewater.

## Comments

(1)	QC results calculated from raw data. Results may vary slightly if the rounded values are used in the calculations.
(2)	Soil, Sludge, and Plant matrices for Inorganic analyses are reported on a dry weight basis.
(3)	Animal matrices for Inorganic analyses are reported on an "as received" basis.
(4)	An asterisk in the "XQ" column indicates there is an extended qualifier and/or certification qualifier associated with the result.
(5)	If the MDL equals the PQL or the MDL column is omitted, the PQL is the reporting limit.

For a complete list of ACZ's Extended Qualifiers, please click:

<https://acz.com/wp-content/uploads/2019/04/Ext-Qual-List.pdf>

**HECLARIO**

ACZ Project ID: **L80005**

NOTE: If the Rec% column is null, the high/low limits are in the same units as the result. If the Rec% column is not null, then the high/low limits are in % Rec.

**Alkalinity as CaCO3**

SM2320B - Titration

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565378</b>													
WG565378PBW	PBW	05/03/23 15:01				4.7	mg/L		-20	20			
WG565378LCSW3	LCSW	05/03/23 15:19	WC230414-1	820.0001		811.9	mg/L	99	90	110			
L80112-03DUP	DUP	05/03/23 18:44			94.5	110.6	mg/L				16	20	
WG565378LCSW6	LCSW	05/03/23 19:02	WC230414-1	820.0001		821.5	mg/L	100	90	110			

**Aluminum, total recoverable**

M200.8 ICP-MS

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565312</b>													
WG565312ICV	ICV	05/02/23 18:00	MS230410-7	.1		.1021	mg/L	102	90	110			
WG565312ICB	ICB	05/02/23 18:02				U	mg/L		-0.015	0.015			
WG565233LRB	LRB	05/02/23 18:03				U	mg/L		-0.011	0.011			
WG565233LFB	LFB	05/02/23 18:05	MS230414-2	.050065		.0454	mg/L	91	85	115			
L80005-01LFM	LFM	05/02/23 18:36	MS230414-2	.050065	U	.0484	mg/L	97	70	130			
L80005-01LFMD	LFMD	05/02/23 18:38	MS230414-2	.050065	U	.0462	mg/L	92	70	130	5	20	

**Arsenic, total recoverable**

M200.8 ICP-MS

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565312</b>													
WG565312ICV	ICV	05/02/23 18:00	MS230410-7	.05		.05154	mg/L	103	90	110			
WG565312ICB	ICB	05/02/23 18:02				U	mg/L		-0.0006	0.0006			
WG565233LRB	LRB	05/02/23 18:03				U	mg/L		-0.00044	0.00044			
WG565233LFB	LFB	05/02/23 18:05	MS230414-2	.0501		.04747	mg/L	95	85	115			
L80005-01LFM	LFM	05/02/23 18:36	MS230414-2	.0501	U	.0485	mg/L	97	70	130			
L80005-01LFMD	LFMD	05/02/23 18:38	MS230414-2	.0501	U	.04713	mg/L	94	70	130	3	20	

**Cadmium, dissolved**

M200.8 ICP-MS

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565842</b>													
WG565842ICV	ICV	05/11/23 16:14	MS230410-7	.05		.052509	mg/L	105	90	110			
WG565842ICB	ICB	05/11/23 16:16				U	mg/L		-0.00011	0.00011			
WG565842LFB	LFB	05/11/23 16:19	MS230428-4	.05005		.050569	mg/L	101	85	115			
L80013-04AS	AS	05/11/23 16:35	MS230428-4	.05005	.00276	.058119	mg/L	111	70	130			
L80013-04ASD	ASD	05/11/23 16:37	MS230428-4	.05005	.00276	.058612	mg/L	112	70	130	1	20	

**Calcium, dissolved**

M200.7 ICP

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565311</b>													
WG565311ICV	ICV	05/02/23 17:39	II230427-2	100		99	mg/L	99	95	105			
WG565311ICB	ICB	05/02/23 17:45				U	mg/L		-0.3	0.3			
WG565311LFB	LFB	05/02/23 17:57	II230417-2	67.98753		66.89	mg/L	98	85	115			
L80003-01AS	AS	05/02/23 18:09	II230417-2	67.98753	92.1	155.5	mg/L	93	85	115			
L80003-01ASD	ASD	05/02/23 18:12	II230417-2	67.98753	92.1	155.4	mg/L	93	85	115	0	20	

**HECLARIO**

ACZ Project ID: **L80005**

NOTE: If the Rec% column is null, the high/low limits are in the same units as the result. If the Rec% column is not null, then the high/low limits are in % Rec.

**Copper, dissolved**

M200.8 ICP-MS

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565842</b>													
WG565842ICV	ICV	05/11/23 16:14	MS230410-7	.05		.05257	mg/L	105	90	110			
WG565842ICB	ICB	05/11/23 16:16				U	mg/L		-0.00176	0.00176			
WG565842LFB	LFB	05/11/23 16:19	MS230428-4	.05005		.04931	mg/L	99	85	115			
L80013-04AS	AS	05/11/23 16:35	MS230428-4	.05005	.00404	.05144	mg/L	95	70	130			
L80013-04ASD	ASD	05/11/23 16:37	MS230428-4	.05005	.00404	.0533	mg/L	98	70	130	4	20	

**Fluoride**

SM4500F-C

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG566104</b>													
WG566104ICV	ICV	05/15/23 13:01	WC230511-1	2.002		2.04	mg/L	102	90	110			
WG566104ICB	ICB	05/15/23 13:05				U	mg/L		-0.3	0.3			
WG566104LFB	LFB	05/15/23 13:12	WC221227-7	5.02		4.95	mg/L	99	90	110			
L80112-02AS	AS	05/15/23 13:36	WC221227-7	5.02	U	5.39	mg/L	107	90	110			
L80112-02ASD	ASD	05/15/23 13:40	WC221227-7	5.02	U	5.31	mg/L	106	90	110	1	20	

**Iron, dissolved**

M200.8 ICP-MS

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG566374</b>													
WG566374ICV	ICV	05/18/23 16:24	MS230410-7	.10016		.1024	mg/L	102	90	110			
WG566374ICB	ICB	05/18/23 16:26				U	mg/L		-0.0154	0.0154			
WG566374LFB	LFB	05/18/23 16:29	MS230428-4	.04995		.0572	mg/L	115	85	115			
L80013-02AS	AS	05/18/23 17:02	MS230428-4	.04995	U	.06	mg/L	120	70	130			
L80013-02ASD	ASD	05/18/23 17:04	MS230428-4	.04995	U	.0571	mg/L	114	70	130	5	20	

**Iron, total recoverable**

M200.8 ICP-MS

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565312</b>													
WG565312ICV	ICV	05/02/23 18:00	MS230410-7	.10016		.1006	mg/L	100	90	110			
WG565312ICB	ICB	05/02/23 18:02				U	mg/L		-0.021	0.021			
WG565233LRB	LRB	05/02/23 18:03				U	mg/L		-0.0154	0.0154			
WG565233LFB	LFB	05/02/23 18:05	MS230414-2	.04995		.0485	mg/L	97	85	115			
L80005-01LFM	LFM	05/02/23 18:36	MS230414-2	.04995	U	.0531	mg/L	106	70	130			
L80005-01LFMD	LFMD	05/02/23 18:38	MS230414-2	.04995	U	.0503	mg/L	101	70	130	5	20	

**Lead, dissolved**

M200.8 ICP-MS

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565842</b>													
WG565842ICV	ICV	05/11/23 16:14	MS230410-7	.05		.05324	mg/L	106	90	110			
WG565842ICB	ICB	05/11/23 16:16				U	mg/L		-0.00022	0.00022			
WG565842LFB	LFB	05/11/23 16:19	MS230428-4	.05005		.05078	mg/L	101	85	115			
L80013-04AS	AS	05/11/23 16:35	MS230428-4	.05005	.0003	.05519	mg/L	110	70	130			
L80013-04ASD	ASD	05/11/23 16:37	MS230428-4	.05005	.0003	.05593	mg/L	111	70	130	1	20	



**HECLARIO**

ACZ Project ID: **L80005**

NOTE: If the Rec% column is null, the high/low limits are in the same units as the result. If the Rec% column is not null, then the high/low limits are in % Rec.

**Magnesium, dissolved**

M200.7 ICP

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565311</b>													
WG565311ICV	ICV	05/02/23 17:39	II230427-2	100		97.58	mg/L	98	95	105			
WG565311ICB	ICB	05/02/23 17:45				U	mg/L		-0.6	0.6			
WG565311LFB	LFB	05/02/23 17:57	II230417-2	49.99752		48.68	mg/L	97	85	115			
L80003-01AS	AS	05/02/23 18:09	II230417-2	49.99752	11.1	59.76	mg/L	97	85	115			
L80003-01ASD	ASD	05/02/23 18:12	II230417-2	49.99752	11.1	60.01	mg/L	98	85	115	0	20	

**Manganese, dissolved**

M200.8 ICP-MS

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565842</b>													
WG565842ICV	ICV	05/11/23 16:14	MS230410-7	.05		.05392	mg/L	108	90	110			
WG565842ICB	ICB	05/11/23 16:16				U	mg/L		-0.00088	0.00088			
WG565842LFB	LFB	05/11/23 16:19	MS230428-4	.04995		.05231	mg/L	105	85	115			
L80013-04AS	AS	05/11/23 16:35	MS230428-4	.04995	.153	.2114	mg/L	117	70	130			
L80013-04ASD	ASD	05/11/23 16:37	MS230428-4	.04995	.153	.21321	mg/L	121	70	130	1	20	

**Mercury, total**

M1631E, Atomic Fluorescence

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG562868</b>													
WG562868ICV	ICV	03/28/23 10:46	HG230302-4	10		10.1	ng/L	101	79	121			
WG562868ICB	ICB	03/28/23 10:51				U	ng/L		-0.501	0.501			
<b>WG564802</b>													
WG564802CCV1	CCV	04/25/23 9:07	HG230302-4	10		10	ng/L	100	76.5	123.4			
WG564802CCB1	CCB	04/25/23 9:12				U	ng/L		-0.501	0.501			
WG564802PQV	PQV	04/25/23 9:17	HG230302-6	1		.92	ng/L	92	70	130			
WG564802LFB1	LFB	04/25/23 9:22	HG230302-5	2		2.02	ng/L	101	71	125			
WG564802CCV2	CCV	04/25/23 10:05	HG230302-4	10		9.71	ng/L	97	76.5	123.4			
WG564802CCB2	CCB	04/25/23 10:09				U	ng/L		-0.501	0.501			
L79989-01MS	MS	04/25/23 10:43	HG230302-5	2	6.13	7.57	ng/L	72	71	125			
L79989-01MSD	MSD	04/25/23 10:47	HG230302-5	2	6.13	7.93	ng/L	90	71	125	5	24	
WG564802CCV3	CCV	04/25/23 11:02	HG230302-4	10		9.4	ng/L	94	76.5	123.4			
WG564802CCB3	CCB	04/25/23 11:07				U	ng/L		-0.501	0.501			
WG564802LFB2	LFB	04/25/23 11:40	HG230302-5	2		1.74	ng/L	87	71	125			
WG564802CCV4	CCV	04/25/23 11:59	HG230302-4	10		9.23	ng/L	92	76.5	123.4			
WG564802CCB4	CCB	04/25/23 12:04				U	ng/L		-0.501	0.501			
WG564802CCV5	CCV	04/25/23 12:29	HG230302-4	10		9.35	ng/L	94	76.5	123.4			
WG564802CCB5	CCB	04/25/23 12:33				U	ng/L		-0.501	0.501			

**Nitrate/Nitrite as N**

M353.2 - Automated Cadmium Reduction

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG564894</b>													
WG564894ICV	ICV	04/25/23 23:35	WI230301-5	2.416		2.28	mg/L	94	90	110			
WG564894ICB	ICB	04/25/23 23:37				U	mg/L		-0.02	0.02			
WG564894LFB	LFB	04/25/23 23:40	WI230228-3	2		1.997	mg/L	100	90	110			
L80005-01AS	AS	04/25/23 23:44	WI230228-3	2	U	2.069	mg/L	103	90	110			
L80030-01DUP	DUP	04/25/23 23:47			9.9	9.911	mg/L				0	20	

**HECLARIO**

ACZ Project ID: **L80005**

NOTE: If the Rec% column is null, the high/low limits are in the same units as the result. If the Rec% column is not null, then the high/low limits are in % Rec.

**Nitrite as N**

**M353.2 - Automated Cadmium Reduction**

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG564894</b>													
WG564894ICV	ICV	04/25/23 23:35	WI230301-5	.608		.603	mg/L	99	90	110			
WG564894ICB	ICB	04/25/23 23:37				U	mg/L		-0.01	0.01			
WG564894LFB	LFB	04/25/23 23:40	WI230228-3	1		1.015	mg/L	102	90	110			
L80005-01AS	AS	04/25/23 23:44	WI230228-3	1	U	1.023	mg/L	102	90	110			
L80030-01DUP	DUP	04/25/23 23:47			U	U	mg/L				0	20	RA

**pH (lab)**

**SM4500H+ B**

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565378</b>													
WG565378LCSW1	LCSW	05/03/23 15:05	PCN623461	5.99		6	units	100	5.9	6.1			
L80112-03DUP	DUP	05/03/23 18:44			8.1	8.1	units				0	20	
WG565378LCSW4	LCSW	05/03/23 18:48	PCN623461	5.99		6	units	100	5.9	6.1			

**Selenium, total recoverable**

**M200.8 ICP-MS**

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565312</b>													
WG565312ICV	ICV	05/02/23 18:00	MS230410-7	.05		.05092	mg/L	102	90	110			
WG565312ICB	ICB	05/02/23 18:02				U	mg/L		-0.0003	0.0003			
WG565233LRB	LRB	05/02/23 18:03				U	mg/L		-0.00022	0.00022			
WG565233LFB	LFB	05/02/23 18:05	MS230414-2	.05005		.04593	mg/L	92	85	115			
L80005-01LFM	LFM	05/02/23 18:36	MS230414-2	.05005	.00239	.04969	mg/L	95	70	130			
L80005-01LFMD	LFMD	05/02/23 18:38	MS230414-2	.05005	.00239	.0473	mg/L	90	70	130	5	20	

**Sulfate**

**D516-02/-07/-11 - TURBIDIMETRIC**

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565693</b>													
WG565693ICB	ICB	05/10/23 10:27				U	mg/L		-3	3			
WG565693ICV	ICV	05/10/23 10:27	WI230427-6	19.54		19.4	mg/L	99	90	110			
L79998-03DUP	DUP	05/10/23 10:40			24.7	24.5	mg/L				1	20	
L79998-04AS	AS	05/10/23 10:40	WI230119-9	10	8.8	20.8	mg/L	120	90	110			M1
WG565693LFB	LFB	05/10/23 11:04	WI230119-9	10		10.2	mg/L	102	90	110			

**Zinc, dissolved**

**M200.8 ICP-MS**

ACZ ID	Type	Analyzed	PCN/SCN	QC	Sample	Found	Units	Rec%	Lower	Upper	RPD	Limit	Qual
<b>WG565842</b>													
WG565842ICV	ICV	05/11/23 16:14	MS230410-7	.05		.0506	mg/L	101	90	110			
WG565842ICB	ICB	05/11/23 16:16				U	mg/L		-0.0132	0.0132			
WG565842LFB	LFB	05/11/23 16:19	MS230428-4	.050075		.0547	mg/L	109	85	115			
L80013-04AS	AS	05/11/23 16:35	MS230428-4	.050075	.532	.5934	mg/L	123	70	130			
L80013-04ASD	ASD	05/11/23 16:37	MS230428-4	.050075	.532	.5933	mg/L	122	70	130	0	20	

Rio Grande Silver, Inc.

ACZ Project ID: **L80005**

ACZ ID	WORKNUM	PARAMETER	METHOD	QUAL	DESCRIPTION
L80005-01	WG564894	Nitrate/Nitrite as N	M353.2 - Automated Cadmium Reduction	HC	Initial analysis within holding time. Reanalysis was past holding time, which was required due to a QC failure during the initial analysis.
			M353.2 - Automated Cadmium Reduction	ZU	Analysis date/time preceeds filter date/time. A portion of sample was filtered and analyzed prior to the creation of a Filter workgroup.
		Nitrite as N	M353.2 - Automated Cadmium Reduction	HC	Initial analysis within holding time. Reanalysis was past holding time, which was required due to a QC failure during the initial analysis.
			M353.2 - Automated Cadmium Reduction	RA	Relative Percent Difference (RPD) was not used for data validation because the concentration of the duplicated sample is too low for accurate evaluation (< 10x MDL).
			M353.2 - Automated Cadmium Reduction	ZU	Analysis date/time preceeds filter date/time. A portion of sample was filtered and analyzed prior to the creation of a Filter workgroup.
	WG565693	Sulfate	D516-02/-07/-11 - TURBIDIMETRIC	M1	Matrix spike recovery was high, the recovery of the associated control sample (LCS or LFB) was acceptable.

**Rio Grande Silver, Inc.**

ACZ Project ID: **L80005**

Metals Analysis

The following parameters are not offered for certification or are not covered by NELAC certificate #ACZ.

Iron, dissolved	M200.8 ICP-MS
Iron, total recoverable	M200.8 ICP-MS

Rio Grande Silver, Inc.

ACZ Project ID: L80005

Date Received: 04/21/2023 10:20

Received By:

Date Printed: 4/24/2023

**Receipt Verification**

	YES	NO	NA
1) Is a foreign soil permit included for applicable samples?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
2) Is the Chain of Custody form or other directive shipping papers present?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
3) Does this project require special handling procedures such as CLP protocol?	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
4) Are any samples NRC licensable material?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
5) If samples are received past hold time, proceed with requested short hold time analyses?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
6) Is the Chain of Custody form complete and accurate?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
7) Were any changes made to the Chain of Custody form prior to ACZ receiving the samples?	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>

**Samples/Containers**

	YES	NO	NA
8) Are all containers intact and with no leaks?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
9) Are all labels on containers and are they intact and legible?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
10) Do the sample labels and Chain of Custody form match for Sample ID, Date, and Time?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
11) For preserved bottle types, was the pH checked and within limits? <sup>1</sup>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
12) Is there sufficient sample volume to perform all requested work?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
13) Is the custody seal intact on all containers?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
14) Are samples that require zero headspace acceptable?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
15) Are all sample containers appropriate for analytical requirements?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
16) Is there an Hg-1631 trip blank present?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
17) Is there a VOA trip blank present?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
18) Were all samples received within hold time?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

NA indicates Not Applicable

**Chain of Custody Related Remarks**

**Client Contact Remarks**

**Shipping Containers**

Cooler Id	Temp (°C)	Temp Criteria (°C)	Rad (µR/Hr)	Custody Seal Intact?
7169	1.5	<=6.0	15	Yes

Was ice present in the shipment container(s)?

Yes - Wet ice was present in the shipment container(s).

Client must contact an ACZ Project Manager if analysis should not proceed for samples received outside of their thermal preservation acceptance criteria.

Rio Grande Silver, Inc.

ACZ Project ID: L80005

Date Received: 04/21/2023 10:20

Received By:

Date Printed: 4/24/2023

<sup>1</sup> The preservation of the following bottle types is not checked at sample receipt: Orange (oil and grease), Purple (total cyanide), Pink (dissolved cyanide), Brown (arsenic speciation), Sterile (fecal coliform), EDTA (sulfite), HCl preserved vial (organics), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> preserved vial (organics), and HG-1631 (total/dissolved mercury by method 1631).





# Site Specific Tiered Standards Segments 4a and 7 from CCR 1002-36

- (5) The acute(warm) cadmium equation applies to segments classified as Aquatic Life Warm Class 1 or 2. The acute(cold) cadmium equation applies to segments classified as Aquatic Life Cold Class 1 or 2.
- (6) Unless the stable forms of chromium in a waterbody have been characterized and shown not to be predominantly chromium VI, data reported as the measurement of all valence states of chromium combined should be treated as chromium VI. In addition, in no case can the sum of the concentrations of chromium III and chromium VI or data reported as the measurement of all valence states of chromium combined exceed the water supply standards of 50 µg/L chromium in those waters classified for domestic water use.
- (7) Selenium is a bioaccumulative metal and subject to a range of toxicity values depending upon numerous site-specific variables.

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(4) Site-Specific Standards, Assessment Locations, and Assessment Criteria

- (a) Seasonal Aluminum Standards for Alamosa River/La Jara Creek/Conejos River Segment 8, Terrace Reservoir:

5/1-6/30 Near Surface:

Aluminum(chronic)=873(T) µg/L  
Aluminum(acute)=TVS(T) µg/L  
Aluminum(chronic)=59 µg/L  
Aluminum(acute)=159 µg/L

5/1-6/30 Near Bottom:

Aluminum(chronic)=1,542(T) µg/L  
Aluminum(acute)=5,583(T) µg/L  
Aluminum(chronic)=41 µg/L  
Aluminum(acute)=65 µg/L

7/1-4/30 Near Surface:

Aluminum(chronic)=102(T) µg/L  
Aluminum(acute)=TVS(T) µg/L  
Aluminum(chronic)=9 µg/L  
Aluminum(acute)=15 µg/L

7/1-4/30 Near Bottom:

Aluminum(chronic)=227(T) µg/L  
Aluminum(acute)= TVS(T) µg/L  
Aluminum(chronic)=9 µg/L  
Aluminum(acute)=12 µg/L

- (b) Site-specific standards and assessment locations for Rio Grande Segment 4a:

**Standards effective through 12/31/2023**

Low flow (August 1-March 31):

Cadmium(chronic)=0.50 µg/L  
Manganese(chronic)=WS  
Zinc(acute/chronic)=257 / 164 µg/L

High flow (April 1-July 31):

Cadmium(chronic)=0.42 µg/L  
Manganese(chronic)=WS  
Zinc(acute/chronic)=115 / 88 µg/L

**Tier 1 standards effective 1/1/2024 through 12/31/2025**

Low flow (August 1-March 31):

Cadmium(chronic)=0.49 µg/L  
Manganese(chronic)=81 µg/L  
Zinc(acute/chronic)=253 / 162 µg/L

High flow (April 1-July 31):

Cadmium(chronic)=0.42 µg/L  
Manganese(chronic)=WS  
Zinc(acute/chronic)=115 / 88 µg/L

**Tier 2 standards effective from 1/1/2026**

Low flow (August 1-March 31):

Cadmium(chronic)=TVS  
Manganese(chronic)=WS  
Zinc(acute/chronic)=142 / 64 µg/L

High flow (April 1-July 31):

Cadmium(chronic)=TVS  
Manganese(chronic)=WS  
Zinc(acute/chronic)=51 µg/L / TVS

**Assessment Locations:** For assessing the standards on Segment 4a, data from the following three locations will be combined:

- Station RG-4: Rio Grande downstream of Highway 149 bridge near Wason Ranch (37.821943, -106.889589)
- Station RG-8: Rio Grande upstream of Highway 149 bridge near La Garita Ranch Drive (37.777672, -106.836631)
- Station RG-9: Rio Grande downstream of 4 UR/Goose Creek Road bridge (37.765798, -106.830305)

(c) Site-specific standards and assessment locations for Rio Grande Segment 7:

**Standards effective through 12/31/2023**

**West Willow**

Low flow (August 1-March 31):

Cadmium(acute/chronic)=32.6 / 27.4 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=108 / 102 µg/L  
Manganese(acute/chronic)=3,320 / 2,425 µg/L  
Zinc(acute/chronic)=11,960 / 9,360 µg/L

High flow (April 1-July 31):

Cadmium(acute/chronic)=22.5 / 15.5 µg/L  
Copper(acute/chronic)=34.3 / 28.0 µg/L  
Lead(acute/chronic)=TVS / 23.5 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=4,001 / 3,765 µg/L

**Windy Gulch**

Low flow (August 1-March 31):

Cadmium(acute/chronic)=13.3 / 13.3 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / TVS  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=3,584 / 3,492 µg/L

High flow (April 1-July 31):

Cadmium(acute/chronic)=7.1 / 5.9 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / 1.68 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=1,940 / 1,558 µg/L

**Willow Creek**

Low flow (August 1-March 31):

Cadmium(acute/chronic)=20.9 / 16.9 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / 24.4 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=5,861 / 5,427 µg/L

High flow (April 1-July 31):

Cadmium(acute/chronic)=10.9 / 8.5 µg/L  
Copper(acute/chronic)=11.2 / 8.2 µg/L  
Lead(acute/chronic)=TVS / 14.2 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=2,667 / 1,873 µg/L

**Tier 1 standards effective 1/1/2024 through 12/31/2025**

**West Willow**

Low flow (August 1-March 31):

Cadmium(acute/chronic)=32.6 / 27.4 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=108 / 102 µg/L  
Manganese(acute/chronic)=3,320 / 2,425 µg/L  
Zinc(acute/chronic)=11,960 / 9,360 µg/L

High flow (April 1-July 31):

Cadmium(acute/chronic)=22.5 / 15.5 µg/L  
Copper(acute/chronic)=34.3 / 28.0 µg/L  
Lead(acute/chronic)=TVS / 23.5 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=4,001 / 3,765 µg/L

**Windy Gulch**

Low flow (August 1-March 31):

Cadmium(acute/chronic)=13.3 / 13.3 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / TVS  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=3,584 / 3,492 µg/L

High flow (April 1-July 31):

Cadmium(acute/chronic)=7.1 / 5.9 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / 1.68 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=1,940 / 1,558 µg/L

**Willow Creek**

Low flow (August 1-March 31):

Cadmium(acute/chronic)=14.4 / 11.6 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / 17.0 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=4,041 / 3,743 µg/L

High flow (April 1-July 31):

Cadmium(acute/chronic)=9.5 / 7.4 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / 12.5 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=2,324 / 1,635 µg/L

**Tier 2 standards effective from 1/1/2026**

**West Willow**

Low flow (August 1-March 31):

Cadmium(acute/chronic)=19.1 / 13.0 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=68.2 / 61.2 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=6,055 / 3,011 µg/L

High flow (April 1-July 31):

Cadmium(acute/chronic)=14.9 / 7.7 µg/L  
Copper(acute/chronic)=27.0 / 20.5 µg/L  
Lead(acute/chronic)=TVS / 9.5 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=2,498 / 2,254 µg/L

**Windy Gulch**

Low flow (August 1-March 31):

Cadmium(acute/chronic)=13.3 / 13.3 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / TVS  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=3,584 / 3,492 µg/L

High flow (April 1-July 31):

Cadmium(acute/chronic)=7.1 / 5.9 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / 1.68 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=1,940 / 1,558 µg/L

**Willow Creek**

Low flow (August 1-March 31):

Cadmium(acute/chronic)=14.9 / 11.1 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / 7.7 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=3,521 / 3,106 µg/L

High flow (April 1-July 31):

Cadmium(acute/chronic)=6.3 / 4.0 µg/L  
Copper(acute/chronic)=TVS / TVS  
Lead(acute/chronic)=TVS / 6.0 µg/L  
Manganese(acute/chronic)=TVS / TVS  
Zinc(acute/chronic)=1,758 / 974 µg/L

**Assessment Locations:**

**West Willow**

- Station WW-A (WW-1): West Willow just above East Willow Confluence (37.864431, -106.925529)

**Windy Gulch**

- Station WNG-A: Windy Gulch at mouth (37.856498, -106.928140)